

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-291814

(43)Date of publication of application : 04.11.1998

---

(51)Int.Cl. C01B 31/02  
// B01J 19/12

---

(21)Application number : 09-103063

(71)Applicant : RIKAGAKU KENKYUSHO

(22)Date of filing : 21.04.1997

(72)Inventor : OYAMA TOSHIYUKI  
TAKEUCHI KAZUO  
OSAWA SHUICHI

---

### (54) SYNTHESIZING METHOD OF FULLERENE

#### (57)Abstract:

**PROBLEM TO BE SOLVED:** To synthesize fullerene without including hetero-nuclide capable of using various carbon sources and dispensing with a sensitizing agent by causing a breakdown reaction by irradiating a gaseous hydrocarbon compd. with a laser beam.

**SOLUTION:** A hydrocarbon compd. in a vapor phase state is irradiated hourly and spacially with a laser beam high in brightness. In this way, even the laser beam having a wavelength in which the hydrocarbon compd. does not indicate absorption is adsorbed to the hydrocarbon compd. and the hydrocarbon compd. in the vapor phase state causes a breakdown reaction (dielectric breakdown). As the result, fullerene are produced. The laser beam causing the dielectric breakdown reaction and high in brightness hourly and spacially is changed according to a kind of the subject gas and a wavelength of the laser, but for example, is the laser beam of about 106-109 W/cm<sup>2</sup>. The hydrocarbon compd. to be used as a starting material is not specifically limited and a degree of freedom in a starting material selection is high.

---

### LEGAL STATUS

[Date of request for examination] 27.03.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3379886

[Date of registration] 13.12.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

**\* NOTICES \***

**JPO and NCIPi are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**CLAIMS**

---

[Claim(s)]

[Claim 1] The synthetic approach of the fullerene characterized by making fullerene generate by irradiating laser light at a gas-like hydrocarbon compound, and making a breakdown reaction cause.

[Claim 2] The synthetic approach according to claim 1 of being one sort or two sorts or more of compounds chosen from the group which a hydrocarbon compound becomes from aromatic hydrocarbon, saturation or partial saturation aliphatic hydrocarbon and saturation, or partial saturation alicyclic hydrocarbon.

[Claim 3] Laser is a pulse YAG laser, an excimer laser, and a pulse CO<sub>2</sub>. The synthetic approach according to claim 1 or 2 of being laser or copper steamy laser.

---

[Translation done.]

**\* NOTICES \***

**JPO and NCIPi are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the synthetic approach of the fullerene using a laser breakdown reaction.

[0002]

[Description of the Prior Art] Fullerene is the matter of the hollow which consists of the football's carbon represented by C<sub>60</sub>. Some kinds of C<sub>70</sub> grades are known as what exists in stability besides C<sub>60</sub>. Furthermore, it is also known that fullerene will carry out inclusion of the metal to the interior of the hollow, and these metal clathrate compound attracts attention as matter in which a new property is shown. Moreover, it is also known that the thin film of fullerene has a nonlinear optics property, and the utilization as a nonlinear optical element is also expected.

[0003]

[Problem(s) to be Solved by the Invention] Generating, when carbon burns is known and fullerene mainly has the laser evaporation method in heating flow gas, a resistance heating method, and an arc discharge method as the process. However, from a viewpoint of mass production method, the arc discharge method effectiveness is high is used. By the arc discharge method, fullerene is compounded by making two graphite inter-electrode cause arc discharge. Also in the laser evaporation method in heating flow gas, and a resistance heating method, a raw material is graphite. Although there is a thermal decomposition method about the naphthalene which pyrolyzes the combustion method which burns the mixed gas of benzene and oxygen, and naphthalene as an approach using raw materials other than graphite, the carbon source is restricted to benzene or naphthalene.

[0004] By the way, this invention person proposed the manufacture approach of the hetero fullerene by laser gaseous phase reaction previously as the new synthetic approach of fullerene [JP,6-80411,A]. By this approach, the hetero fullerene which uses elements other than carbon as different nuclear species is manufactured by irradiating laser light and carrying out induction of the gaseous phase reaction to the mixed gas containing the 1st raw material which consists of unsaturated hydrocarbon, and the 2nd raw material containing elements other than a carbon atom. In this approach, the 2nd raw material containing elements other than the carbon atom as a sensitizer to which said laser light can be absorbed and induction of the gaseous phase reaction can be carried out is indispensable. Induction of the gaseous phase reaction is not carried out without a sensitizer. Moreover, such a sensitizer is for example, a boron compound, and is using a boron compound as a sensitizer, and the hetero fullerene which uses boron as different nuclear species generates it.

[0005] Since the 2nd raw material which contains elements other than the carbon atom as a sensitizer by this approach is indispensable, composition of the fullerene which does not include different nuclear species is difficult. That is, it is difficult to obtain the fullerene which does not include different nuclear species, without using a sensitizer in the above-mentioned laser gaseous phase reaction.

[0006] Then, the object of this invention is to offer the synthetic approach of the fullerene which can obtain the fullerene which it is possible to use various carbon sources, and does not need to use a sensitizer, and does not include different nuclear species.

[0007]

[Means for Solving the Problem] This invention relates to the synthetic approach of the fullerene characterized by making fullerene generate by irradiating laser light at a gas-like hydrocarbon compound, and making a breakdown reaction cause.

[0008]

[The mode of implementation of invention] Generally, when the pulsed light of laser is irradiated at a gas, and the energy per laser photometric-units area (particle fluence) is small, laser luminous energy is hardly absorbed by the gas. However, if the laser light of the above reinforcement is irradiated to some extent at a gas, gaseous dielectric breakdown (gas breakdown) will arise for the time and spatial high brightness of laser light. With respect to gaseous absorption wavelength, there is nothing and most irradiated laser energies are absorbed by gaseous dielectric breakdown. The approach of compounding the particle of boron carbide (B<sub>4</sub>C), using the laser breakdown method is learned [JP,3-215309,A].

[0009] above to the hydrocarbon compound which is in a gaseous-phase condition by the approach of this invention -- the laser light of high brightness is irradiated in time and spatially. Thereby, even if a hydrocarbon compound is the laser of the wavelength which does not show absorption, it is absorbed by the hydrocarbon compound and, as for the hydrocarbon compound of a gaseous-phase condition, breakdown, i.e., a dielectric-breakdown reaction, is started. Consequently, fullerene generates. Although the laser light of high brightness changes with the wavelength of the class of target gas when a dielectric-breakdown reaction is caused, or laser etc. in time and spatially, they are about 10<sup>6</sup> - 10<sup>9</sup> W/cm<sup>2</sup>, for example. It is the laser light of the reinforcement of the range.

[0010] There is especially no limit in the hydrocarbon compound used as a raw material. Since the existence of absorption to laser does not become the factor which determines the fitness as a raw material at least, the degree of freedom of raw material selection is high. Hydrocarbon compounds can be one sort or two sorts or more of compounds chosen from the group which consists of aromatic hydrocarbon, saturation or partial saturation aliphatic hydrocarbon and saturation, or partial saturation alicyclic hydrocarbon. However, since the object product is a carbon compound (fullerene) which does not contain hydrogen, the lower one of the hydrogen/carbon rate in a raw material is desirable from viewpoints, such as yield. Therefore, as for the coal-for-coke-making-ized hydride, it is desirable that they are aromatic hydrocarbon, partial saturation aliphatic hydrocarbon, and partial saturation alicyclic hydrocarbon.

[0011] As for aromatic hydrocarbon, polycyclic-type aromatic hydrocarbon, such as benzene, and the derivative, naphthalene, etc. is mentioned. Moreover, as partial saturation aliphatic hydrocarbon, acetylene, ethylene, a propene, a butene, a butadiene, an allene, etc. can be mentioned. Cyclobutene, cyclopentene, a cyclohexene, etc. can be mentioned as partial saturation alicyclic hydrocarbon.

[0012] As laser, if breakdown is produced, there will be especially no limit in conditions, such as the light source and wavelength. As laser, they are a pulse YAG laser, an excimer laser, and a pulse CO<sub>2</sub>, for example. Laser or copper steamy laser can be mentioned.

[0013] The approach of this invention can be enforced using the equipment shown in drawing 1. Among drawing, one shows a glass reaction container, the introductory tubing 2 for introducing gas into the reaction container 1 interior is formed in the upper part of the reaction container 1, and a cock 3 intervenes between the introductory tubing 2 and the reaction container 1. Moreover, the entrance window of laser light which consists of KBr etc. is prepared in the flank of the reaction container 1. the laser light 7 which 5 is the laser light source and is irradiated from the output aperture 6 of the laser light source 5 -- BaF<sub>2</sub> etc. -- from -- it is condensed by the gas of the reaction container 1 interior with the becoming lens 8. The laser light source 5 can be chosen from various laser, such as a pulse YAG laser, as mentioned above.

[0014] By the approach of this invention, in order to make a breakdown reaction cause, it is necessary to irradiate the laser light of the reinforcement more than fixed per an unit area and unit time amount. Then, when determining the reinforcement of the laser light source, since laser light is condensed in a gas raw material while taking this point into consideration, a convex lens 8 is used as mentioned above. The approach of this invention can also be enforced under the temperature below a room temperature, and temperature up in consideration of the vapor pressure of a raw material etc. while being able to perform it at a room temperature. Moreover, the class of raw material, the class of laser, reinforcement, etc. can determine time amount required for a reaction conclusion suitably. Usually, it is a 60-minute about room.

[0015] According to the approach of this invention, not only C<sub>60</sub> but high order fullerene (for example, C<sub>70</sub> and C<sub>84</sub> grade) can also be collectively compounded so that the mass spectrum shown in the example may also show. It has the description that the generation ratio of the high order fullerene especially to C<sub>60</sub> is high. A product can obtain the target fullerene by carrying out separation purification suitably by the well-known

approach.

[0016]

[Effect of the Invention] According to this invention, the synthetic approach of the fullerene which can obtain the fullerene which does not include different nuclear species can be offered, without using a sensitizer using various carbon sources.

[0017]

[Example] Hereafter, an example explains this invention further.

In the equipment shown in example 1 drawing 1, the 3l. reaction container 1 was filled up with the benzene steam of 50Torr(s), and laser light was irradiated at the room temperature, using a pulse Nd:YAG laser (1064nm, 1 J/pulse 10Hz) as the laser light source 5 (laser light on-the-strength  $4 \times 10^7$  W/cm<sup>2</sup>). When laser light was irradiated, the light and the sound which show that the breakdown reaction arose were made. Products were collected after reaction termination. The mass spectrum of a product is shown in drawing 2. m/z720 equivalent to C<sub>60</sub> was begun, and the peak was looked at by m/z equivalent to the high order fullerene of C<sub>70</sub> and C<sub>84</sub> grade. As a result of checking a product with liquid chromatography furthermore, existence of C<sub>60</sub> and C<sub>70</sub> was checked from the retention time.

[0018] Example benzene of reference (C<sub>6</sub>H<sub>6</sub>) Instead, it is an example 1 except having used C<sub>6</sub>D<sub>6</sub> or <sup>13</sup>C<sub>6</sub>H<sub>6</sub>. The breakdown reaction was performed on the same conditions. The mass spectrum of a product is shown in drawing 3 (raw material C<sub>6</sub>D<sub>6</sub>) and drawing 4 (raw material <sup>13</sup>C<sub>6</sub>H<sub>6</sub>). The result of drawing 3 is substantially [ as the result of drawing 2 ] the same, and the product by the approach of this invention suggested that it was the compound which does not contain hydrogen. Moreover, by the result of drawing 4, it is <sup>13</sup>C. The peak which is in agreement with the mass number of fullerene was acquired. These results all show that it is the fullerene which the product of the breakdown reaction in the approach of this invention becomes only from carbon.

---

[Translation done.]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

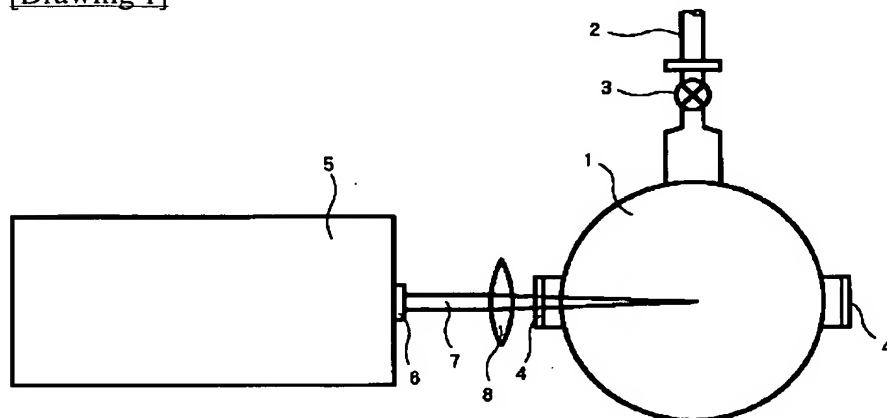
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

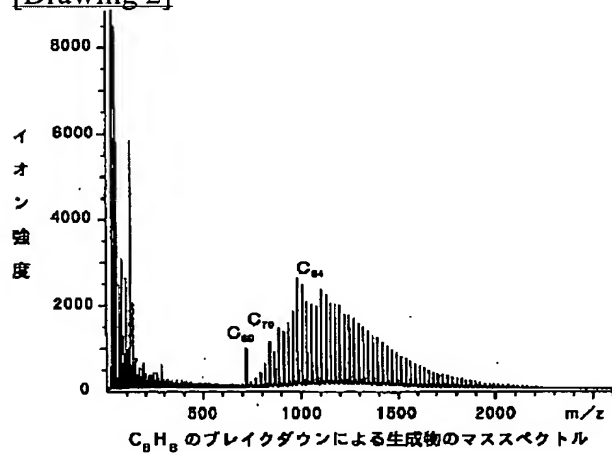
DRAWINGS

---

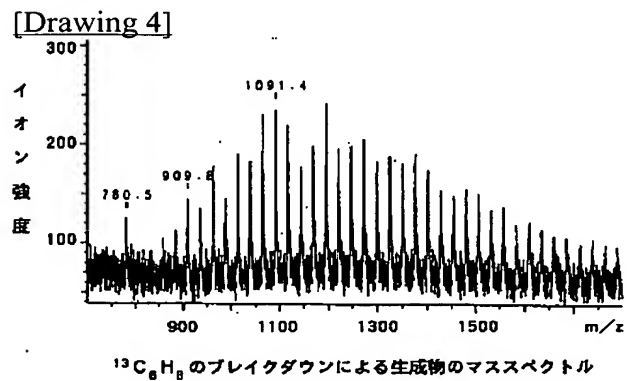
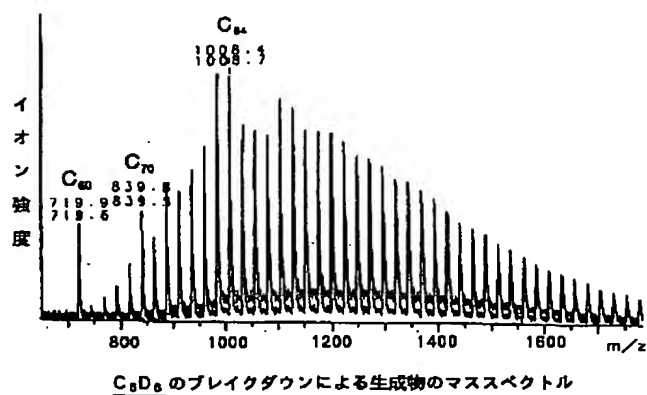
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]